

Towards a full Heusler alloy showing room temperature half-metallicity at the surface

M Cinchetti¹, J-P Wüstenberg¹, M Sánchez Albaneda¹, F Steeb¹, A Conca², M Jourdan², M Aeschlimann¹

¹University of Kaiserslautern, Institute of Physics, Erwin-Schrödingerstr. 46, 67663 Kaiserslautern, Germany

²University of Mainz, Institute of Physics, Staudinger Weg 7, 55128 Mainz, Germany

E-mail: cinchett@rhrk.uni-kl.de

Abstract. In this article we investigate the surface spin polarization in a 100 nm $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ (CCFA) film grown *ex situ* epitaxially on $\text{MgO}(100)$ with a 10 nm Fe buffer layer by means of spin resolved photoemission. We show that a careful *in situ* preparation of the sample surface leads to values for the room temperature spin polarization up to 45% at the Fermi level. To our knowledge, this is the highest value measured so far at the surface region of a full Heusler alloy at room temperature.

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1. Introduction

The success of modern spintronics devices, i.e. devices relying on the electron spin as carrier of information depends crucially on the ability to store, transport and manipulate the spin state of an electron within a properly chosen material system. While storage is traditionally accomplished by the use of magnetoresistive effects in magnetic multilayer systems, the latter problems seem to be trackable by the use of (partly) semiconductive materials, where typical spin diffusion lengths are much larger and material properties can be tuned precisely to establish a coupling to external fields for coherent spin manipulation purposes [1]. However, the conductivity mismatch [2, 3] between ferromagnetic metals and semiconductors which hinders efficient spin injection is still an unsolved issue. There are two possible approaches to overcome this issue [4]: realize pure semiconductor devices (for which ferromagnetic semiconductors are needed) or search for new materials exhibiting large carrier spin polarization. A promising class of materials for the latter possibility consists of half metallic Heusler alloys, exhibiting metallic behavior for one spin direction and a band gap for the other. This should lead to a full spin polarization P at the Fermi level E_F , which is more generally defined as the ratio of spin up and spin down electron occupation numbers with respect to a certain energy and given quantization axis:

$$P(E) = \frac{N_{up}(E) - N_{down}(E)}{N_{up}(E) + N_{down}(E)} \quad (1)$$

In order to be attractive for technical applications, a Heusler alloy should satisfy in principle three requirements: such a material should show a full polarization: (i) at E_F (i.e., be a half-metal), (ii) not only in bulk but up to the very surface region, and (iii) at room temperature.

The fabrication quality of such alloys is improving steadily. This is shown for example in the case of Co_2FeSi by the increasing coherence between measured and predicted values for the element-specific number of magnetic moments μ_B per unit cell [5, 6]. However, the connection to the spin polarization at E_F as the relevant parameter is not straightforward and relies heavily on the chosen model potential in calculations.

To our knowledge, a Heusler compound satisfying all conditions (i),(ii) and (iii) has not yet been reported. Half metallicity has been experimentally verified in NiMnSb but only for the bulk material and at $T = 27\text{ K}$ [7]. On the other hand, surface sensitive techniques failed to demonstrate half-metallicity of such compound. It is not straightforward that the surface region of a Heusler alloy will show the same electron spin polarization (ESP) as the bulk material. In principle, extrinsic as well as intrinsic mechanism may reduce the spin polarization at the surface. Among the extrinsic mechanisms, chemical and magnetic disorder have been discussed to play a relevant role [8, 9]. Intrinsic mechanisms, that take place also at perfectly ordered surfaces, are for example magnetic fluctuations and modifications in the surface band structure with respect to the bulk one. In a recent publication, Kolev *et al.* [10] have investigated the (100) surface of NiMnSb using spin-resolved appearance potential spectroscopy and

found a significantly reduced spin asymmetry with respect to calculations based on the bulk electronic structure. By a careful analysis, the authors could exclude chemical disorder, structural defects at the surface, as well as overall stoichiometric disorder as responsible mechanisms for the observed reduction of spin polarization. In another paper Wang *et al.* [11] have studied single-crystalline Co_2MnSi films and found for $P(E_F)$ a maximal value of 12% measured with spin-resolved photoemission at room temperature. They attribute this high discrepancy with the expected value of 100% to partial chemical disorder in the Co_2MnSi lattice.

$\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ (CCFA) has been intensively studied both experimentally [12, 13, 14, 15, 16, 17, 18] and theoretically [19, 20, 21]. The interest in this compound is due to its high Curie temperature of 760 K and its theoretically predicted high value of volume magnetization of $3.8 \mu_B$ per formula unit [22]. To our knowledge, the spin-resolved photoemission results presented here for thin films of such full Heusler compound set the actual room temperature ESP record for Heusler alloys to 45% at the Fermi level and at the surface region, a value reflecting the increasing sample quality as well as more and more sophisticated surface preparation methods. This constitutes a very important step towards the goal of producing an alloy satisfying simultaneously conditions (i), (ii) and (iii).

2. Experimental setup

The thin films samples are prepared in a commercial MBE deposition system with analysis chamber which is complemented by a home build sputter chamber.

The spin-resolved photoemission experiments are performed in a separate UHV system with a base pressure of $< 10^{-10}$ mbar, equipped with an Ar^+ sputter gun. Surface characterization is achieved by LEED as well as Auger analysis and by identifying characteristic features of the photoemission spectrum. The latter is obtained by irradiating the sample with the s-polarized 4th harmonic (photon energy 5.9 eV) of a 100 fs Ti:Sapphire oscillator (Spectra Physics Tsunami). The laser light angle of incidence is set by geometry to 45° , while the spectra are taken in normal electron emission. Spin resolved photoemission spectra are recorded by a commercial cylindrical sector analyzer (Focus CSA 300) equipped with an additional spin detector based on spin-polarized low-energy electron diffraction (Focus SPLEED). The achieved energy resolution is 150 meV, the acceptance angle of the analyzer is $\pm 13^\circ$. For the measurements the films are remanently magnetized by an external in-plane magnetic field.

3. Sample preparation and pre-characterization

The thin films of $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ were deposited by dc magnetron sputtering from a stoichiometric target. Epitaxial growth in (100) orientation was obtained on $\text{MgO}(100)$ substrates employing an Fe buffer layer (10 nm thickness). X-ray diffraction analysis

revealed that the films grow in the B2 structure. The sample surface after deposition and annealing is well ordered as demonstrated by electron diffraction (RHEED)[23]. To protect the surface of the 100 nm thick Heusler-film from oxidation during the transport between the preparation and the photoemission chamber, the sample was capped by 4 nm of Al.

Before characterization with spin resolved photoemission, the magnetic properties of the sample were studied *ex situ* using magneto-optical Kerr effect. A fourfold in-plane anisotropy was reported [24], reflecting the crystallographic symmetry of the CCFA film.

4. In situ sample treatment

In order to obtain reproducible results with spin resolved photoemission, the (100) surface of the the sample has to be carefully prepared *in situ*. Since this experimental technique is sensitive to the surface region [25], the protecting Al cap-layer has to be carefully removed. A further reason requiring a careful preparation is that the crystal structure of CCFA easily allows for atomic disorder, either by interchange of atoms or by partial occupancy [12].

Due to the critical role played by the preparation procedure, we will describe it in detail.

- (A) As first step the Al cap-layer was removed from the sample by several cycles of Ar^+ ion sputtering at moderate rates (sputtering energy 500 eV at an angle of incidence of $\pm 65^\circ$ with respect to the surface normal). The successful removal of the cap layer was checked by means of Auger spectroscopy and by monitoring the changes in the photoemission spectrum.
- (B) The sample was heated at 300°C for 12 hours before the first characterization attempts.
- (C) Without further treatment, the prepared surface shows no LEED patterns, and the measured polarization is identically zero over the whole spectral range of about 2 eV below E_F .
- (D) As a next step the sample was treated with further sputtering and heating (at 300°C) cycles until a clear LEED pattern was observable.
- (E) For the last cycles the sample temperature was held at 300°C during Ar^+ ion sputtering. After sputtering the sample was heat flashed for approx. 1 min. to 450°C . The last step was repeated before each measurement, and assures the reproducibility of the obtained results.

5. Experimental results and discussion

Figure 1 (a) shows a LEED image obtained from the sample after the steps (A) to (D) of the *in situ* preparation procedure described in Section 4. The picture was recorded at 88 eV primary electron energy and demonstrates a clear fourfold symmetry

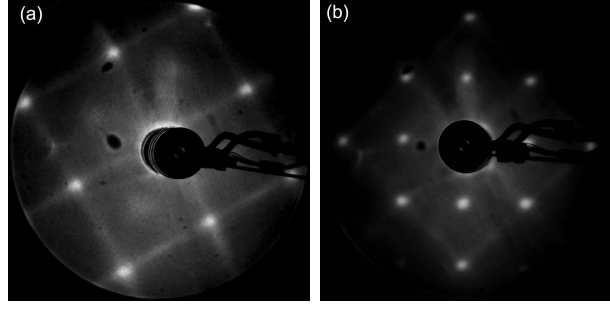


Figure 1. (a) LEED pattern of the sample after the steps (A) to (D) of the *in situ* preparation procedure, taken at 88 eV primary electron energy. (b) LEED pattern of the sample after the full *in situ* preparation procedure (steps (A) to (E)) , taken at 100 eV primary electron energy.

in correspondence with the cubic bulk lattice. If step (E) is also applied, then the LEED pattern obtained from the sample is shown in Figure 1 (b). The picture was recorded at 100 eV primary electron energy. Compared to Figure 1 (a), Figure 1 (b) shows a clearer LEED pattern, demonstrating that the preparation step (E) leads to a better rearrangement of the surface atoms.

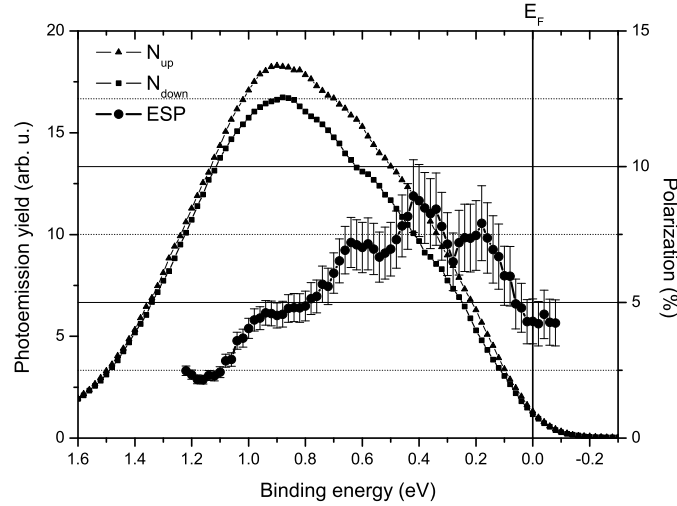


Figure 2. Spin resolved photoemission spectra and ESP of the CCFA thin film after preparation steps (A) to (D).

Left scale: photoemission yield from majority electrons (N_{up}) with filled triangles and minority electrons (N_{down}) with filled squares.

Right scale: ESP as obtained from Equation (1), with filled circles.

Figure 2 shows on the left scale the spin resolved photoemission spectra recorded from CCFA after after the steps (A) to (D) of the *in situ* preparation procedure described in Section 4, i.e. corresponding to the LEED pattern of Figure 1 (a). The spectra for

the majority electrons (N_{up}) are represented with filled triangles, the one for minority electrons (N_{down}) with filled squares. They show the Fermi level E_F (showing up at 0 eV in the chosen binding energy scale) and a monotonous increase of the photoemission yield up to ~ 0.9 eV. The low energy cutoff is approximately at 1.2 eV. The ESP, calculated from those two curves using Equation (1), is shown in the same picture on the right scale (filled circles). Overall, the ESP does not reach values higher than 10%. In particular, it starts from 2.5% at the low energy cutoff, and shows three peaks at 0.6 eV, 0.4 eV and 0.2 eV. Then, it decreases again towards E_F to reach $P(E_F) \sim 5\%$, well below the expected value of 100%.

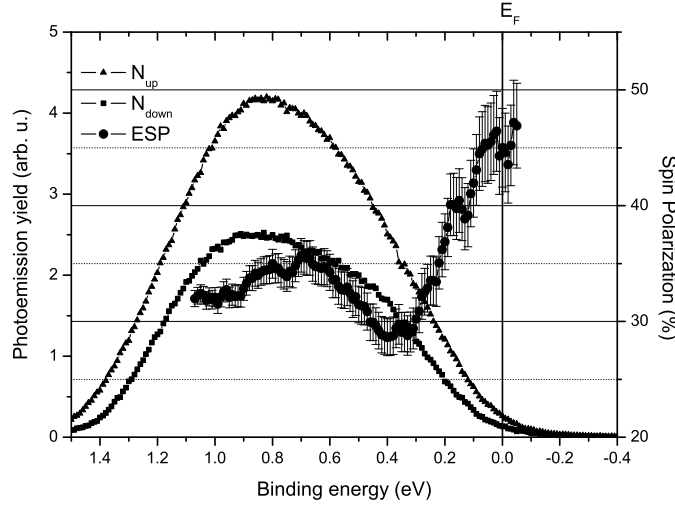


Figure 3. Spin resolved photoemission spectra and ESP of the CCFA thin film after the full preparation procedure (steps (A) to (E)).

Left scale: photoemission yield from majority electrons (N_{up}) with filled triangles and minority electrons (N_{down}) with filled squares.

Right scale: ESP as obtained from Equation (1), with filled circles.

Figure 3 shows on the left scale the spin resolved photoemission spectra recorded from CCFA after the full *in situ* preparation procedure (steps (A) to (E)), i.e. corresponding to the LEED pattern of Figure 1 (b). Again, the spectra for the majority electrons are represented with filled triangles, the one for minority electrons with filled squares. In this case, the two spectra have remarkably different intensities, resulting in the ESP depicted with filled circles on the right scale. Between the low energy cutoff (~ 1.1 eV) and 0.4 eV binding energy, the ESP assumes values between approximately 35% and 30%, then it increases more or less steadily and reaches the value $P(E_F) \sim 45\%$. This value is to our knowledge the highest spin polarization at the surface region reported so far by means of spin resolved photoemission from a full Heusler alloy at room temperature. The remarkable difference in the absolute value and energy dependence of the ESP in Figure 2 and Figure 3 is a clear indication for the extreme importance of the

surface preparation procedure prior to the measurements. Indeed, Correa *et al.* [26] have reported for the half Heusler alloy NiMnSb(100), that an optimized annealing process after sputtering is essential to restore the bulk stoichiometry of the surface, disturbed by the previous sputtering. Evidence for such behavior was taken from the analysis of normal-emission ultraviolet photoemission spectra.

The specific surface treatment employed in our paper is the result of an empirical optimization of the surface preparation prior to the measurements, aimed to reach the highest possible value of the surface spin polarization. The achieved results show that for this particular Heusler alloy, the reduction of the surface spin polarization can be -at least partially- circumvented by selecting an adequate preparation procedure. This is of course very important also for the production of spintronics devices, where surface and interface between different materials play a crucial role for the injection of spin polarization.

The increasing of the ESP towards E_F in Figure 3 is a clear indication for the presence of a band gap (at least partial) for the minority electrons, as expected from theoretical calculations [21]. However, at this point we have to notice that photoemission from a single crystal gives information only about direct transitions taking place near the surface Brillouin zone center. Thus, the comparison of our experimental data with density of states (DOS) calculations, as the one reported in [21], can be only qualitative. Further angle- and spin-resolved measurements are planned in the next future. Together with band structure calculations (including correlations effects) this will give further precious information about the electronic band structure of the CCFA Heusler alloy.

6. Conclusions

In this paper we have found an optimized preparation procedure for the (100) surface of the full Heusler alloy $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$. Applying such procedure, we have obtained a room temperature surface spin polarization of 45% at the Fermi level by means of spin resolved photoemission. To our knowledge, this is the highest value reported so far by means of a surface sensitive experimental technique. We proposed that implementing such a procedure could lead to a better performance of spintronics devices based on Heusler alloys.

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